Supporting Information for

Slow magnetic relaxation and spin crossover behavior in two mixed-valence Co(II)/Co(III) complexes

Contents of the Supporting Information

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Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Elemental analyses were measured on a PerkinElmer analyzer model 240. IR spectra were performed in pressed KBr pellets on a Bruker Tensor 27 spectrophotometer. The thermogravimetric analyses (TGA) of **1** and **2** were carried out on a NETZSCH TG209F3 instrument under flowing N_2 at a heating rate of 10 K min^{-1} between 300 and 1000 K. Power X-Ray diffraction (PXRD) patterns were recorded on a MiniFlex-600 diffractometer (Cu-Kα, λ = 1.54056 Å), and the simulated patterns were obtained by Mercury 3.10 software. Magnetic measurements were performed using Quantum Design PPMS SQUID magnetometer. Samples were sealed in parafilm to avoid any orientation of the crystallites. Samples were wrapped in tinfoil. The magnetic data were corrected for the sample holder and diamagnetic contributions.

X-ray crystallography and data collection

Single-crystal diffraction data of **1** and **2** were collected by an XtaLAB Synergy R, DW system HyPix diffractometer diffractometer using a mirror mono-chromated Cu-Kα radiation. Data reduction, scaling and absorption corrections were performed using CrysAlisPro. The structure were solved using intrinsic phasing methods (SHELXT) and by using Olex2 as the graphical interface.[1] The model was refined with olex2 refine using full matrix least squares minimisation on F^2.[2] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. CCDC 2174565-2174568 contains the supplementary crystallographic data for this paper. The crystallographic data and refinement parameters for **1** and **2** are listed in Table S1 and Table S4, respectively. For complex **2**, lattice solvent molecules are disorder. We have used solvent mask to deal with this problem.

Table S1. Crystallographic parameter for complex **1**.

	Complex_**1**
Empirical formula	$C_{184}H_{164}Co_6N_{66}O_{29}$
Formula weight	4117.38
Temperature/K	213.99(11)
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	16.2176(4)
b/Å	17.0260(3)
c/Å	17.2151(3)
α/°	82.777(2)
β/°	75.137(2)
γ/°	83.919(2)
Volume/Å^3	4544.47(17)
Z	1
ρ_{calc}g/cm^3	1.504
μ/mm^{-1}	4.957
F(000)	2124.0
2θ range for data collection/°	5.248 to 153.956
Reflections collected	62426
Independent reflections	18417 [Rint = 0.0945, Rsigma = 0.0905]
Data/restraints/parameters	18417/6/1340
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R1 = 0.0759, wR2 = 0.2015
Final R indexes [all data]	R1 = 0.0973, wR2 = 0.2247
Largest diff. peak/hole / e Å^{-3}	1.26/-0.51
CCDC	2174565

Table S2. Co–N, Co–O Bond lengths (Å) around Co center and BVS values for Co atom in complex **1** at 214 K.

Complex 1					
Bond	**Bond Length / Å**	**Bond Valence**	**Bond**	**Bond Length / Å**	**Bond Valence**
Co1–N1	2.140(3)	0.321	Co2–O5	1.895(3)	0.498
Co1–N2	2.133(4)	0.328	Co2–O7	1.895(3)	0.498
Co1–N3	2.128(3)	0.332	Co2–N7	1.908(4)	0.555
Co1–N4	2.099(3)	0.359	Co2–N8	1.909(4)	0.553
Co1–N5	2.143(4)	0.319	Co2–N9	1.914(4)	0.546
Co1–N6	2.118(3)	0.341	Co2–N10	1.905(4)	0.559
	∑v(Co) = 2.000			∑v(Co) = 3.209	

Bond	**Bond Length / Å**	**Bond Valence**
Co3-O1	1.898(3)	0.494
Co3-O3	1.900(3)	0.491
Co3–N11	1.900(3)	0.567
Co3–N12	1.889(3)	0.584
Co3–N13	1.891(3)	0.581
Co3–N14	1.898(3)	0.570
	∑v(Co) = 3.287	

Bond Valence = $\exp[(R_0-d_{ij})/b]$, R_0 = 1.720 for Co^{II}–N, 1.637 for Co^{III}–O and 1.690 for Co^{III}–N, b = 0.37.

Table S3. Selected bond angles (°) for complex **1**.

Complex 1					
Bond	Angle / °	Bond	Angle / °	Bond	Angle / °
N1 Co1 N5	91.78(14)	O5 Co2 N10	84.42(14)	O1 Co3 O3	89.23(12)
N2 Co1 N5	169.74(14)	O5 Co2 N9	164.89(15)	O1 Co3 N11	94.99(12)
N2 Co1 N1	78.32(14)	O5 Co2 N7	93.50(14)	N13 Co3 O1	84.79(12)
N3 Co1 N5	92.25(13)	O5 Co2 N8	90.55(15)	N13 Co3 O3	93.34(12)
N3 Co1 N1	95.72(12)	O7 Co2 O5	89.39(13)	N13 Co3 N14	80.42(12)
N3 Co1 N2	91.40(14)	O7 Co2 N10	93.13(14)	N13 Co3 N11	178.45(14)
N4 Co1 N6	97.08(13)	O7 Co2 N9	90.29(15)	N14 Co3 O1	165.17(12)
N4 Co1 N5	97.19(14)	O7 Co2 N7	85.11(13)	N14 Co3 O3	92.79(13)
N4 Co1 N1	169.83(14)	O7 Co2 N8	165.35(14)	N14 Co3 N11	99.82(13)
N4 Co1 N2	92.91(14)	N10 Co2 N9	80.51(16)	N11 Co3 O3	85.12(12)
N4 Co1 N3	79.22(12)	N10 Co2 N7	177.30(15)	N12 Co3 O1	91.24(14)
N6 Co1 N1	89.52(13)	N10 Co2 N8	101.44(16)	N12 Co3 O3	165.95(12)
N6 Co1 N2	99.58(14)	N7 Co2 N9	101.52(16)	N12 Co3 N13	100.69(13)
N6 Co1 N3	168.60(14)	N7 Co2 N8	80.28(15)	N12 Co3 N14	90.34(15)
N6 Co1 N5	77.44(13)	N8 Co2 N9	93.54(16)	N12 Co3 N11	80.85(13)

Table S4. Crystallographic parameters for complex **2** at 100 K、298 K、373 K.

	Complex 2		
Empirical formula		$C_{90}H_{84}Co_3N_{34}O_{13}$	
Formula weight		2026.70	
Temperature/K	100.00(10)	297.99(18)	373.0(3)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.42884(11)	11.5085(4)	11.53950(10)
b/Å	15.20373(10)	15.2210(9)	15.21920(10)
c/Å	28.11736(15)	28.5790(6)	28.7586(2)
α/°	77.2450(5)	77.152(3)	77.0300(10)
β/°	80.0214(6)	80.333(3)	80.5910(10)
γ/°	73.2019(7)	73.050(5)	72.9510(10)
Volume/Å^3	4530.34(6)	4640.2(4)	4679.57(7)
Z	2	2	2
ρ_{calc}g/cm^3	1.486	1.451	1.438
μ/mm^{-1}	4.952	4.835	4.794
F(000)	2094	2094	2094
Reflections collected	63932	63067	54432
Independent reflections	18529 [Rint = 0.0432, Rsigma = 0.0381]	18771[Rint= 0.0566, Rsigma = 0.0460]	18002 [Rint = 0.0306, Rsigma =0.0333]
Data/restraints/parameters	18529/452/1287	18772/111/1282	18002/0/1039
Goodness-of-fit on F^2	1.025	1.089	1.075
Final R indexes [I>=2σ (I)]	R1 = 0.0466, wR2 = 0.1293	R1 = 0.0534, wR2 =0.1574	R1 = 0.0469, wR2 =0.1438
Final R indexes [all data]	R1 = 0.0504, wR2 = 0.1320	R1 = 0.0631, wR2 = 0.1656	R1 = 0.0516, wR2 = 0.1479
Largest diff. peak/hole/e Å^{-3}	0.542/-0.434	0.530/-0.389	0.264/-0.422
CCDC	2174566	2174567	2174568

Table S5. Co–O, Co–N Bond lengths (Å) around Co centers and BVS values for Co atoms in complex **2** at 100 K.

Complex 2					
Bond	**Bond Length / Å**	**Bond Valence**	**Bond**	**Bond Length / Å**	**Bond Valence**
Co1–N1	2.022(2)	0.319	Co2–O1	1.899(16)	0.492
Co1–N2	1.882(19)	0.467	Co2–O3	1.913(16)	0.475
Co1–N3	2.019(19)	0.322	Co2–N7	1.885(19)	0.512
Co1–N4	2.128(2)	0.240	Co2–N12	1.894(18)	0.499
Co1–N5	1.924(19)	0.416	Co2–N13	1.895(19)	0.498
Co1–N6	2.112(2)	0.250	Co2–N18	1.890(18)	0.505
	∑v(Co) = 2.009			∑v(Co) = 2.981	

Bond	**Bond Length / Å**	**Bond Valence**
Co3-O5	1.899(10)	0.493
Co3-O7	1.912(9)	0.476
Co3–N19	1.883(19)	0.514
Co3–N24	1.886(2)	0.51
Co3–N25	1.883(19)	0.509
Co3–N30	1.892(2)	0.501
	∑v(Co) = 3.003	

Bond Valence = $\exp[(R_0-d_{ij})/b]$, R_0 = 1.60 for Co^{II}–N, 1.637 for Co^{III}–O and 1.690 for Co^{III}–N, b = 0.37.

Table S6. Co–O, Co–N Bond lengths (Å) around Co centers in complex **2** at 100 K、298 K、373 K, respectively.

100 K		298 K		373 K	
Bond	**Bond Length / Å**	**Bond**	**Bond Length / Å**	**Bond**	**Bond Length / Å**
Co1–N1	2.022(2)	Co1–N1	2.083(2)	Co1–N1	2.108(2)
Co1–N2	1.8819(19)	Co1–N2	1.940(2)	Co1–N2	1.973(2)
Co1–N3	2.0198(19)	Co1–N3	2.077(2)	Co1–N3	2.102(2)
Co1–N4	2.128(2)	Co1–N4	2.105(2)	Co1–N4	2.117(2)
Co1–N5	1.9243(19)	Co1–N5	1.943(2)	Co1–N5	1.978(2)
Co1–N6	2.112(2)	Co1–N6	2.101(2)	Co1–N6	2.118(2)
Co2–O1	1.8994(16)	Co2–O1	1.9037(18)	Co2–O1	1.8970(17)
Co2–O3	1.9133(16)	Co2–O3	1.9095(19)	Co2–O3	1.9112(18)
Co2–N7	1.8857(19)	Co2–N7	1.888(2)	Co2–N7	1.8874(19)
Co2–N12	1.8943(18)	Co2–N12	1.894(2)	Co2–N12	1.8940(18)
Co2–N13	1.8951(19)	Co2–N13	1.896(2)	Co2–N13	1.896(2)
Co2–N18	1.8906(18)	Co2–N18	1.889(2)	Co2–N18	1.8880(17)
Co3-O5	1.899(10)	Co3-O5	1.8973(19)	Co3-O5	1.8996(17)
Co3-O7	1.912(9)	Co3-O7	1.9014(18)	Co3-O7	1.9035(16)
Co3–N19	1.8828(19)	Co3–N19	1.887(2)	Co3–N19	1.8895(19)
Co3–N24	1.886(2)	Co3–N24	1.884(2)	Co3–N24	1.8892(17)
Co3–N25	1.8863(19)	Co3–N25	1.892(2)	Co3–N25	1.8914(18)
Co3–N30	1.892(2)	Co3–N30	1.889(2)	Co3–N30	1.8880(17)

Table S7. Selected bond angles (°) for complex **2** at 100 K.

Complex 2					
Bond	Angle / °	Bond	Angle / °	Bond	Angle / °
N1 Co1 N4	93.52(8)	O1 Co2 O3	89.94(7)	O5 Co3 O7	91.0(14)
N1 Co1 N6	90.88(8)	N7 Co2 O1	165.80(7)	N19 Co3 O5	170.1(4)
N2 Co1 N1	80.76(8)	N7 Co2 O3	90.76(7)	N19 Co3 O7	89.5(7)
N2 Co1 N3	80.93(8)	N7 Co2 N12	80.92(8)	N19 Co3 N24	80.87(8)
N2 Co1 N4	105.35(8)	N7 Co2 N13	91.75(8)	N19 Co3 N25	90.32(8)
N2 Co1 N5	175.44(8)	N7 Co2 N18	98.58(8)	N19 Co3 N30A	96.89(8)
N2 Co1 N6	96.06(8)	N12 Co2 O1	84.98(7)	N19 Co3 O7A	94.3(7)
N3 Co1 N1	161.53(8)	N12 Co2 O3	99.63(7)	N19 Co3 O5A	162.9(4)
N3 Co1 N4	88.96(7)	N12 Co2 N13	94.87(8)	N24 Co3 O5	89.3(4)
N3 Co1 N6	93.47(8)	N13 Co2 O1	91.12(8)	N24 Co3 O7	90.8(3)
N5 Co1 N1	97.62(8)	N13 Co2 O3	165.49(7)	N24 Co3 N30A	177.75(8)
N5 Co1 N3	100.82(8)	N18 Co2 O1	95.61(7)	N24 Co3 O7A	99.4(4)
N5 Co1 N4	78.96(8)	N18 Co2 O3	84.94(7)	N25 Co3 O5	90.9(11)
N5 Co1 N6	79.67(8)	N18 Co2 N12	175.39(8)	N25 Co3 O7	170.2(4)
N6 Co1 N4	158.57(8)	N18 Co2 N13	80.55(8)	N25 Co3 N24	98.84(8)

Table S8. Selected bond angles (°) for complex **2** at 298K.

Complex 2					
Bond	Angle / °	Bond	Angle / °	Bond	Angle / °
N1 Co1 N4	92.98(9)	O1 Co2 O3	90.16(9)	O5 Co3 O7	88.83(8)
N1 Co1 N6	91.67(9)	N7 Co2 O1	165.30(9)	N19 Co3 O5	166.25(9)
N2 Co1 N1	79.11(9)	N7 Co2 O3	90.23(9)	N19 Co3 O7	92.04(9)
N2 Co1 N3	79.27(9)	N7 Co2 N12	80.55(9)	N19 Co3 N25	90.61(9)
N2 Co1 N4	105.95(9)	N7 Co2 N13	91.89(10)	N19 Co3 N30	96.68(9)
N2 Co1 N5	174.95(10)	N7 Co2 N18	99.14(9)	N24 Co3 O5	85.16(9)
N2 Co1 N6	96.28(9)	N12 Co2 O1	84.88(8)	N24 Co3 O7	95.83(8)
N3 Co1 N1	158.12(10)	N12 Co2 O3	99.20(8)	N24 Co3 N19	81.10(9)
N3 Co1 N4	89.73(9)	N12 Co2 N13	95.49(9)	N24 Co3 N25	98.45(9)
N3 Co1 N6	93.98(9)	N13 Co2 O1	91.46(9)	N24 Co3 N30	177.76(9)
N5 Co1 N1	98.78(9)	N13 Co2 O3	165.30(8)	N25 Co3 O5	91.93(9)
N5 Co1 N3	103.05(9)	N18 Co2 O1	95.53(8)	N25 Co3 O7	165.72(9)
N5 Co1 N4	78.67(9)	N18 Co2 O3	84.77(8)	N30 Co3 O5	97.06(8)
N5 Co1 N6	79.14(9)	N18 Co2 N12	176.01(9)	N30 Co3 O7	84.54(8)
N6 Co1 N4	157.77(10)	N18 Co2 N13	80.53(9)	N30 Co3 N25	81.22(8)

Table S9. Selected bond angles (°) for complex **2** at 373K.

Complex 2					
Bond	Angle / °	Bond	Angle / °	Bond	Angle / °
N1 Co1 N4	92.97(9)	O1 Co2 O3	90.20(8)	O5 Co3 O7	88.57(7)
N1 Co1 N6	92.18(9)	N7 Co2 O1	165.41(8)	N19 Co3 O5	165.98(8)
N2 Co1 N1	78.32(9)	N7 Co2 O3	90.01(8)	N19 Co3 O7	91.93(8)
N2 Co1 N3	78.10(8)	N7 Co2 N12	80.78(8)	N19 Co3 N25	91.06(8)
N2 Co1 N4	107.46(9)	N7 Co2 N13	92.13(9)	N24 Co3 O5	84.98(8)
N2 Co1 N5	174.36(8)	N7 Co2 N18	99.11(8)	N24 Co3 O7	96.30(7)
N2 Co 1 N6	96.40(9)	N12 Co2 O1	84.78(7)	N24 Co3 N19	81.04(8)
N3 Co1 N1	156.11(9)	N12 Co2 O3	99.17(8)	N24 Co3 N25	97.95(8)
N3 Co1 N4	90.42(8)	N12 Co2 N13	95.56(8)	N25 Co3 O5	91.89(8)
N3 Co1 N6	94.21(9)	N13 Co2 O1	91.37(9)	N25 Co3 O7	165.74(7)
N4 Co1 N6	156.13(9)	N13 Co2 O3	165.27(8)	N30 Co3 O5	97.43(7)
N5 Co1 N1	99.55(9)	N18 Co2 O1	95.44(8)	N30 Co3 O7	84.64(7)
N5 Co1 N3	104.28(8)	N18 Co2 O3	84.81(7)	N30 Co3 N19	96.57(8)
N5 Co1 N4	77.77(9)	N18 Co2 N12	176.02(8)	N30 Co3 N2)	177.44(8)
N5 Co1 N6	78.40(9)	N18 Co2 N13	80.46(8)	N30 Co3 N25	81.16(7)

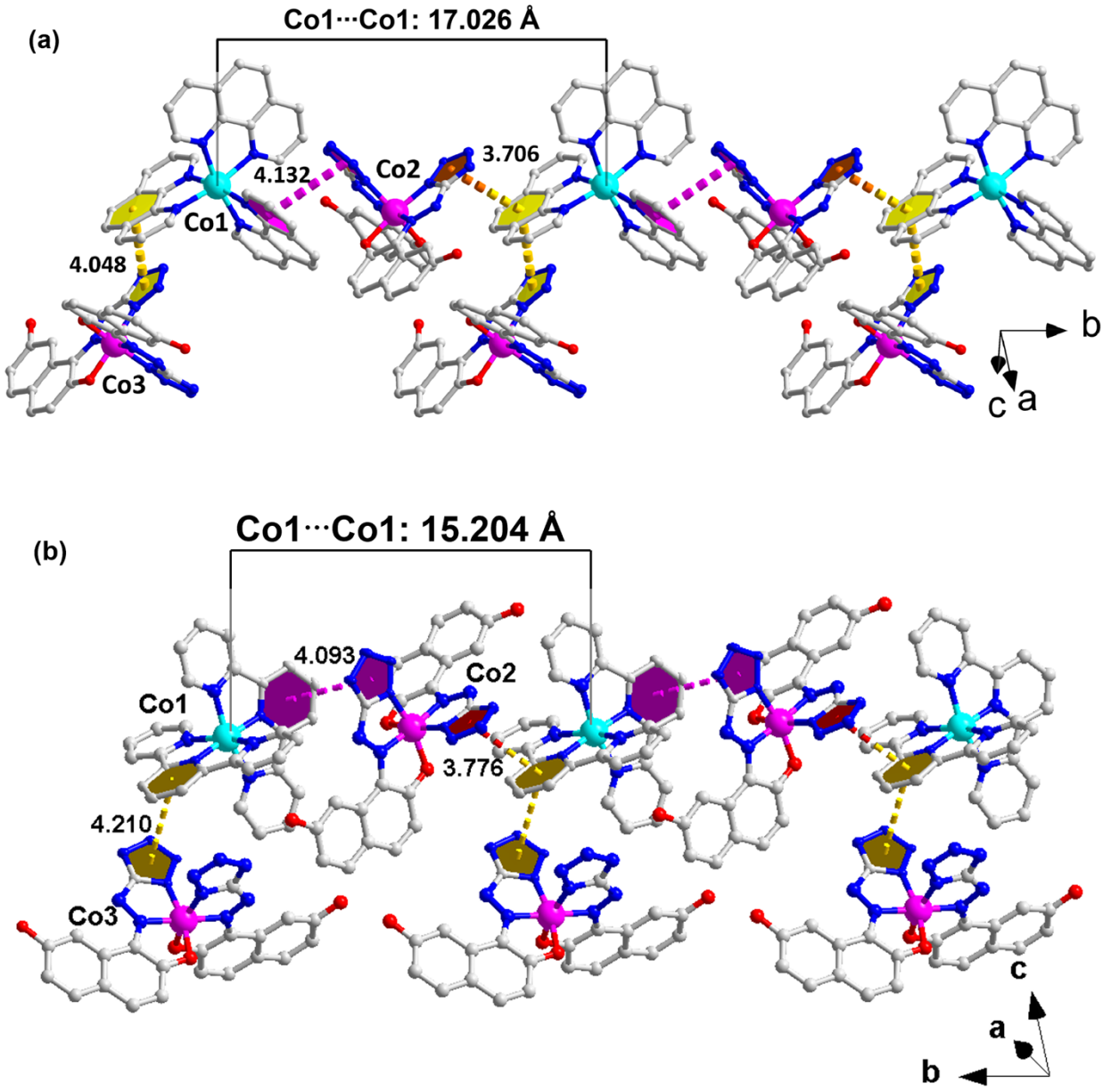

Figure S1 The π–π stacking interaction for complexes **1** (a) and **2** (b).

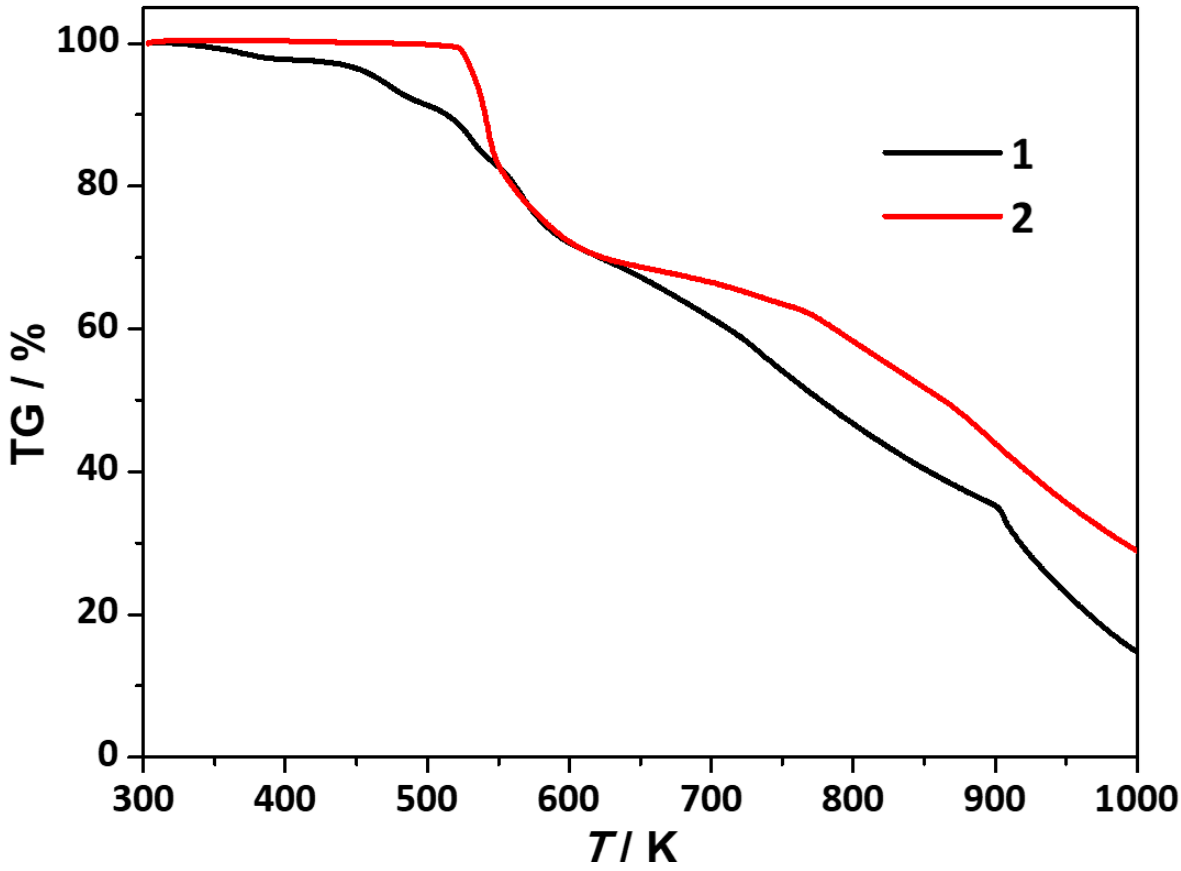

Figure S2 Thermal gravimetric Analyses (TGA) curves for complexes **1** and **2**.

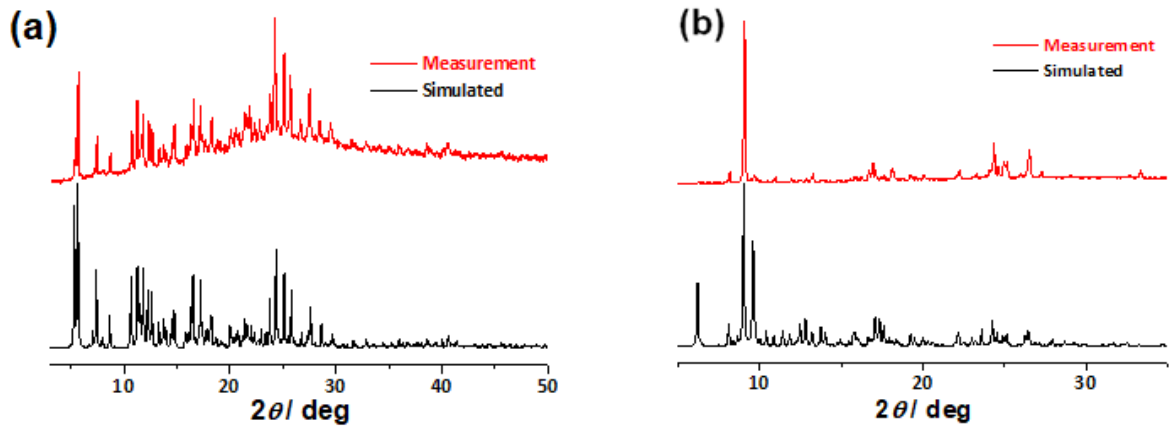

Figure S3 Powder X-ray diffraction (PXRD) patterns for complexes **1** (a) and **2** (b).

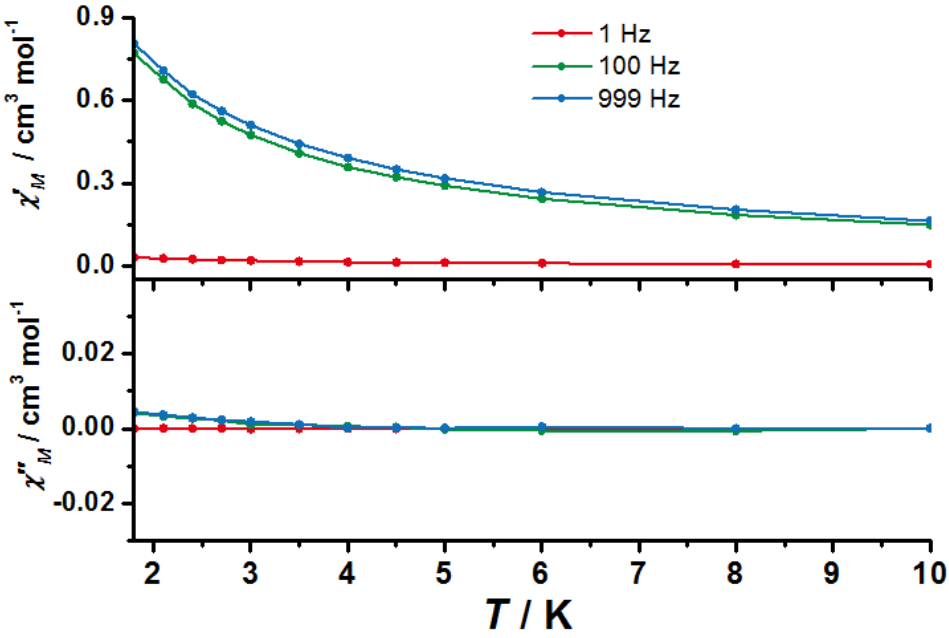

Figure S4 Temperature dependence of the out-of-phase for complex **1** at zero DC-external field.

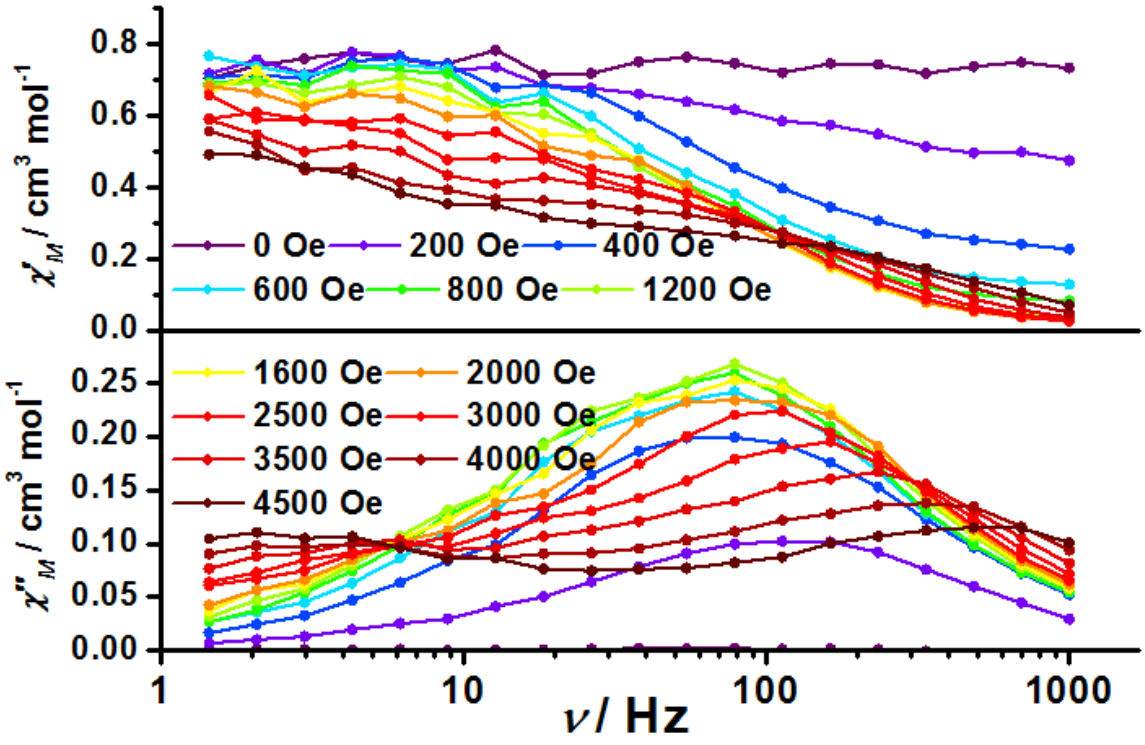

Figure S5 Frequency dependence of χ'_M and χ''_M signals at various fields at 2 K for **1**.

Table S10 Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **1** at 800 Oe field.

T (K)	τ□(s)	α	χ_0 (cm^3 mol^{-1})	χ_∞ (cm^3 mol^{-1})
1.8	0.0034(9)	0.21(2)	0.81(1)	0.057(1)
2.1	0.0025(7)	0.19(2)	0.73(1)	0.048(1)
2.4	0.0017(5)	0.18(2)	0.63(1)	0.043(1)
2.7	0.0012(4)	0.15(2)	0.56(1)	0.042(1)
3.0	0.0009(3)	0.13(2)	0.50(1)	0.041(1)
3.5	0.0005(2)	0.07(2)	0.43(1)	0.046(1)
4.0	0.0003(2)	0.03(2)	0.38(1)	0.044(1)
4.5	0.0002(2)	0.06(2)	0.34(1)	0.023(1)
5.0	0.00005(3)	0.09(2)	0.30(1)	-0.1(1)

Table S11. Compilation of the six-coordinate Co compounds discussed in the text.

Compoud	SIM, *H*=0	SIM, *H*≠0	Ueff/K	τ_0/s	Ref.
$[Co^{II}(phen)_3][Co^{III}(HATD)_2]_2 \cdot 3DMA \cdot 3.5H_2O$	No	800 Oe	22.6	$5.7(5) \times 10^{-7}$	This work
$[Co(SCN)_2(4\text{-}dzbpy]$	Yes	-	89	2.3×10^{-10}	3
$[HNEt_3][Co^{II}Co^{III}{}_3L_6]$	Yes	-	109.06	1×10^{-7}	4
$[Co(Pzox)_3(BC_6H_5)]Cl$	Yes	-	102	-	5
$[Co^{III}Co^{II}(LH_2)_2(Cl)(H_2O)](H_2O)_4$	No	1000 Oe	11.37	6.1×10^{-6}	6
$[Co^{III}Co^{II}(LH_2)_2(Br)(H_2O)](H_2O)_4$	No	1000 Oe	20.86	1×10^{-6}	6
$[Co(12C4)_2](I_3)_2$ (12C4)	No	500 Oe	24.5	1.5×10^{-6}	7
$[Co(L)_4(NO_3)_2]$	No	1000 Oe	14.9	5.6×10^{-6}	8
$[Co(L_1)_2]$	No	2000 Oe	54.9	2.28×10^{-9}	9
$[Co(L_2)_2(CH_3OH)_2]$	No	1000 Oe	24.3	4.89×10^{-7}	9
$[Co(L_3)_2(CH_3OH)_2]$	No	1500 Oe	19.4	2.19×10^{-6}	9
$[(3G)CoCl](CF_3SO_3)$	No	1500 Oe	24	1.9×10^{-10}	10
$[Co(dca)_2(bim)_4]$	No	1000 Oe	7.74	0.87×10^{-6}	11
$[Co(dca)_2(bim)_2]_n$	No	1000 Oe	5.33	1.54×10^{-6}	11
$[Co(dca)_2(bmim)_2]_n$	No	1000 Oe	13.81	0.63×10^{-6}	11
$(NBu_4)[Co(piv)_3]$	No	1000 Oe	20.7	2.69×10^{-8}	12
$[Co(12\text{-}TMC)(NCS)_2] \cdot 0.5CH_3OH$	No	6000 Oe	23.23	3.0×10^{-8}	13
$[Co(12\text{-}TMC)(NCSe)_2] \cdot 0.5CH_3CN$	No	6000 Oe	25.53	1.8×10^{-8}	13
$[Co^{II}(L)_2](ClO_4)_2 \cdot 0.5MeCN \cdot Et_2O$	No	1000 Oe	5.8	1.8×10^{-6}	14
$[Co^{II}(L)(CH_3CN)_2(H_2O)](ClO_4)_2 \cdot MeCN$	No	1000 Oe	20.5	2.7×10^{-7}	14
$[Co(bapen)Br_2]_2[CoBr_4]$	-	-	-	-	15
$[Co^{II}Co^{III}(LH_2)_2(CH_3COO)(H_2O)]$	No	1000 Oe	16.1	7.1×10^{-6}	16

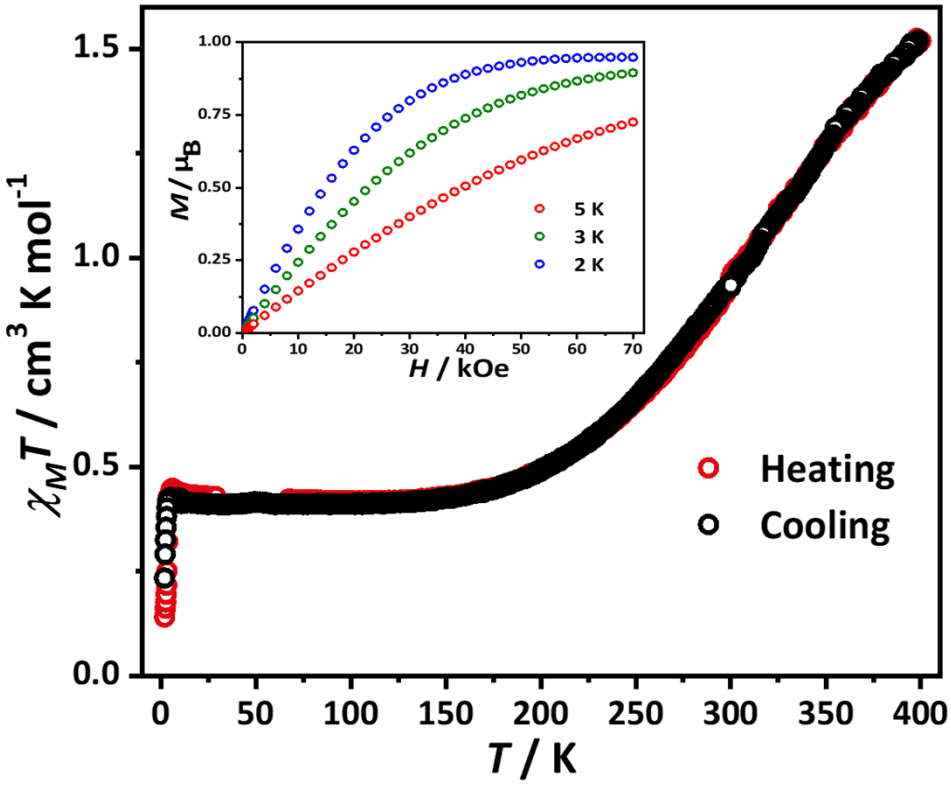

Figure S6 Temperature dependence of $\chi_M T$ vs T plots for complex **2** at 1000 Oe and M vs H plots at 2, 3, 5 K (inset).

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